

# AMENDED SPECIFICATION.

Reprinted as amended in accordance with the decision of the Superintending Examiner, acting for the Comptroller-General, dated the Twenty-second day of November, 1932.

(The Amendments are shown in erased and italic type.)

## PATENT SPECIFICATION



Application Date: May 31, 1930. No. 16,911 / 30.

**354,898**

Complete Left: March 9, 1931.

Complete Accepted: Aug. 20, 1931.

### PROVISIONAL SPECIFICATION.

#### Improvements in and relating to the Manufacture of Photographic Sensitisers.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company incorporated under the laws of Great Britain, and HENRY ALFRED PIGGOTT and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British subjects, do hereby declare the nature of this invention to be as follows:—

Symmetrical and unsymmetrical dye-stuffs of the polymethine series may be obtained by treating the intermediate compounds described in our co-pending Application No. 33,493/29 (Serial No. 344,409) in the absence or presence of a suitable solvent such as ethyl alcohol, pyridine, acetic anhydride, with heterocyclic compounds containing external reactive methylene groups. Thus, for instance,

(1) 15 parts of the compound obtained by the interaction of 2:3:3-trimethylindolenine methiodide and diphenylformamidine and 7 parts of 1:3:3-trimethyl-2-methyleneindoline are boiled together with 250 parts acetic anhydride for one hour. The deep red solution obtained is concentrated by distilling off the solvent. On cooling 1:3:3:1:3:3-hexamethylindocarbocyanine iodide crystallises out. Or

(2) 16 parts of the compound obtained by interaction of quinaldine ethiodide and diphenylformamidine (see Example 2 of Specification No. 344,409) and 7 parts of 1:3:3-trimethyl-2-methylene-indoline are dissolved in 20 parts of acetic anhydride. The solution is boiled under reflux for 10 minutes. It is cooled somewhat, 50 parts of hot water

added and the mixture vigorously stirred. The dyestuff separates and is isolated. Or

(3) 24 parts of the condensation product of 1-methylbenzothiazole ethiodide and diphenylformamidine prepared in a similar manner to Example 1 of Specification No. 344,409 are dissolved by heat in 160 parts acetic anhydride and 18 parts of 2:3:3-trimethylindolinine methiodide added followed by 5 parts anhydrous sodium acetate. The mixture is boiled for 15 minutes, diluted with 150 parts hot water and the precipitated dyestuff purified by lixiviation with ether.

The present invention concerns the application of the said and similar dye-stuffs with the object of rendering photographic emulsions sensitive to light rays in the red and infra-red region of the spectrum. Thus, a standard photographic emulsion is sensitive only from about 360 millimicrons wave-length to 500 millimicrons wave-length. According to the invention we treat a photographic emulsion with the dyestuff prepared as described under (2) above, so that it becomes sensitive over the range of wave-lengths 360 millimicrons to 660 millimicrons. Similarly a photographic emulsion treated with the dyestuff obtained according to (3) above but using 2-methyl benzothiazole ethiodide in place of 2-methyl benzothiazole ethiodide, is sensitive from 360 millimicrons wave-length to 600 millimicrons wave-length.

The treatment is carried out by, for example, bathing the photographic plate in a dilute aqueous alcoholic solution of the dyestuff.

Dated the 31st day of May, 1930.

BEST AVAILABLE COPY

E. A. BINGEN,

Imperial Chemical House, Millbank,  
London, S.W.1,  
Solicitor for the Applicants.

## COMPLETE SPECIFICATION (AMENDED).

## Improvements in and relating to the Manufacture of Photographic Sensitisers.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, and HENRY ALFRED PIAGGOT and ERNEST HARRY RODD, both of Crumpsall Vale Chemical Works, Blackley, Manchester, both British subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

Symmetrical and unsymmetrical dyestuffs of the polymethine series may be obtained by treating the intermediate compounds described in our co-pending Application No. 33493/29 (Serial No. 344,409) in the absence or presence of a suitable solvent such as ethyl alcohol, pyridine, acetic anhydride, with heterocyclic compounds containing external reactive methylene groups. Thus, for instance,

(1) 15 parts of the compound obtained by the interaction of 2:3:3-trimethylindoline methiodide and diphenylformamidine and 7 parts of 1:3:3-trimethyl-2-methyleneindoline are boiled together with 250 parts acetic anhydride for one hour. The deep red solution obtained is concentrated by distilling off the solvent. On cooling 1:3:3:1:31:31-hexamethylindocarbocyanine iodide crystallises out. Or

(2) 16 parts of the compound obtained by interaction of quinaldine ethiodide and diphenyl formamidine (see Example 2 of Specification No. 344,409) and 7 parts of 1:3:3-trimethyl-2-methylene indoline are dissolved in 20 parts of acetic anhydride. The solution is boiled under reflux for 10 minutes. It is cooled somewhat, 50 parts of hot water added and the mixture vigorously stirred.

The dyestuff separates and is isolated. Or  
(2) (3) 24 parts of the condensation product of 1-methylbenzothiazole ethiodide and diphenyl formamidine prepared in a similar manner to Example 1 of Specification No. 344,409 are dissolved by heat in 160 parts acetic anhydride and 18 parts of 2:3:3-trimethylindolinine methiodide added followed by 6 parts anhydrous

sodium acetate. The mixture is boiled for 15 minutes, diluted with 150 parts hot water and the precipitated dyestuff purified by lixiviation with ether.

(3), (4) The compound obtained by interaction of 46 parts of 2:3:3-trimethylindolinine methiodide and diphenylformamidine in acetic anhydride (Example 1 of Specification No. 344,409), 30 parts of 2-methylbenzoxazole ethiodide, and 10 parts of anhydrous potassium acetate are boiled together in 100 parts of acetic anhydride for 1 hour. For the dyestuff, isolated in the usual way, the name 1:3:3-trimethyl-1-ethylindoxacarbocyanine iodide is proposed.

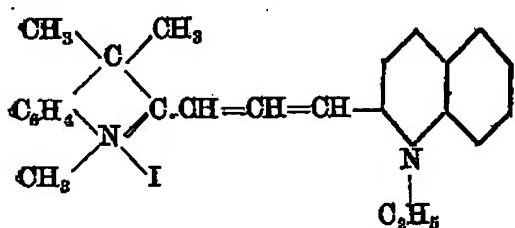
(4) (5) The condensation of the product of interaction of 2-methylbenzothiazole ethiodide and diphenylformamidine prepared as described in Example 5 of Specification No. 344,409 (46 parts) with 2-methylbenzoxazole ethiodide (30 parts) in acetic anhydride in presence of potassium acetate gives an orange dyestuff, for which the name 1:1-diethylthio-oxacarbocyanine iodide is suggested.

According to the present invention we apply the unsymmetrical dyestuffs, e.g., those obtained according to (1), (2), (3) and (4) above to render photographic emulsions sensitive to light-rays in the red and infra-red region of the spectrum.

In carrying our invention into practical effect we treat a photographic emulsion with unsymmetrical dyestuffs described above, e.g. by bathing a photographic plate in a dilute aqueous solution of the dyestuff. Preferably a solution of 1 part of dyestuff in 2000 parts of 50% aqueous alcohol is prepared. The stock solution is diluted for use with about 20 parts of water. 100 cc. of the diluted solution is taken for each photographic plate of whole-plate size to be treated, and the plate is immersed in the solution, which is agitated gently, and kept in contact therewith for a period of about 5 minutes. The plate is then washed with water and dried.

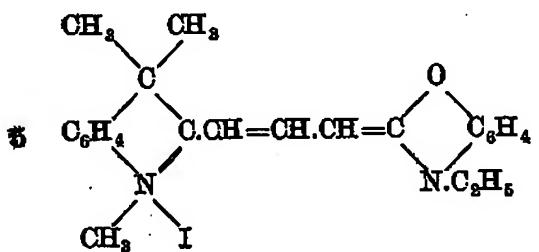
Photographic plates thus treated in accordance with our invention become sensitive as shown in the following table:—

## Formula of dyestuff:—

Wave-length range in  
millimicrons.

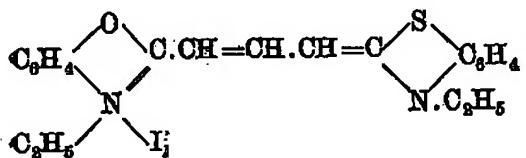
360-653

(prepared as described above under (7 3))



360-600

(prepared as described above under (3-4))



360-640

(prepared as described above under (4 5))

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of photographic emulsions sensitive to light of long wave-length which comprises the application to a photographic emulsion of the unsymmetrical polymethine dyestuffs, hereinbefore specifically substantially as described.

2. Photographic emulsions, sensitive to light of long-wave length whenever obtained by the process of claim 1 or by its obvious chemical equivalent.

3. Photographic plates coated with emulsions as claimed in claim 2.

Dated the 5th day of March, 1931.

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